metal-organic papers

trans-Bis(2-amino-1,3-benzothiazole-κN^3)-dichlorocopper(II)

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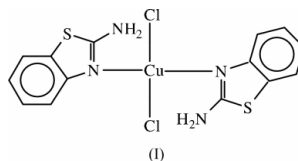Correspondence e-mail: wmaniuk@p.lodz.pl

Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.011 Å
R factor = 0.038
wR factor = 0.087
Data-to-parameter ratio = 9.2

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title complex, $[CuCl_2(C_7H_6N_2S)_2]$, contains a Cu centre with a distorted square-planar coordination geometry, involving two Cl ligands and two endocyclic N atoms from the thiazole moieties [Cu—Cl = 2.275 (2) and 2.297 (2) Å, and Cu—N = 1.986 (5) and 1.988 (5) Å]. The amino groups participate in intra- and intermolecular N—H···Cl hydrogen bonds, with N···Cl distances in the range 3.202 (6)–3.316 (6) Å.

Comment

Aminothiazolines are perceived as an important type of S,N-containing heterocyles (Raper, 1994). Usually, 2-substituted derivatives of 1,3-benzothiazole (2–X–btz; where X is NH_2, CH_3, Cl or S) act as σ-monodentate ligands through the ring N atom (Giusti & Peyronel, 1982). The coordination of 2-aminobenzothiazole (2-abtz) to the M^{II} ions of Co (Macíček et al., 1987), Zn (Usman et al., 2003) and Cu (Sieroń & Bukowska-Strzyżewska, 1999, 2000) has been studied thus far, and those studies confirm that heterocyclic nitrogen-bonded, rather than sulfur-bonded, complexes are found.

(I)

This paper reports the synthesis and crystal structure of a new copper(II) halide complex with 2-abtz, trans-bis(2-amino-1,3-benzothiazole-κN^3)dichlorocopper(II), (I) (Fig. 1), which consists of discrete neutral molecules. These molecules are almost centrosymmetric. The copper centre is coordinated by two Cl ligands and two endocyclic N atoms from the thiazole
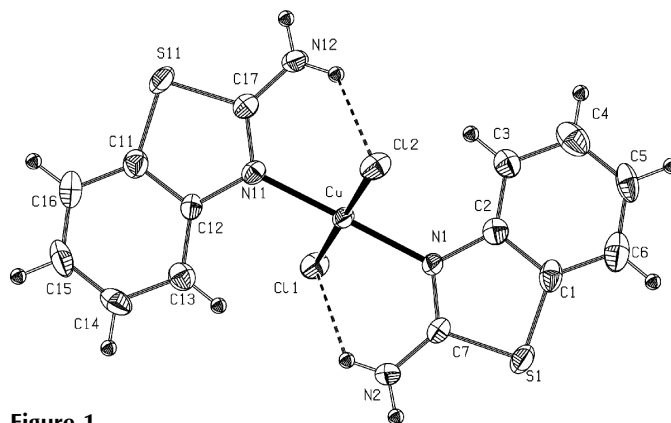

Figure 1
View of (I), with the atom-numbering scheme. Displacement ellipsoids for non-H atoms are drawn at the 50% probability level.

moieties [Cu—Cl = 2.275 (2) and 2.297 (2) Å, and Cu—N = 1.986 (5) and 1.988 (5) Å]. The amino N atoms are not involved in the Cu coordination. Tetrahedral distortion of the square-planar coordination is observed with a tetrahedrality angle θ (Holm & O'Connor, 1971) of 2.6 (2)°. The bond lengths in the 2-abtz ring system (Table 1) are normal (Allen *et al.*, 1987). Due to the pronounced delocalization in the S—C=N fragment of the thiazole ring, the S1—C1 [1.742 (7) Å] and S11—C11 [1.733 (7) Å] bonds are slightly shorter than S1—C7 [1.751 (7) Å] and S11—C17 [1.752 (6) Å]. Also, the bond angles around the endocyclic S atoms are in agreement with the literature values for the geometry around an endocyclic S atom [C1—S1—C7 = 89.6 (3)° and C11—S11—C17 = 89.9 (3)°]. The ligands are planar, with the angles between the mean planes calculated through the five- and six-membered rings of each ligand being 2.4 (3) and 3.4 (3)°. The ligands are almost parallel, with an interplanar angle of 3.8 (2)°. The amino groups are coplanar with the attached thiazole planes. In the crystal packing, each amino group is involved in intra- and intermolecular N—H···Cl hydrogen bonds (Table 2). The N2—H2···Cl1^i and N12—H12···Cl2^{ii} hydrogen bonds interconnect the molecules into chains along the **a** direction (Fig. 2).

Experimental

The title complex was prepared by addition of 0.001 mol of $CuCl_2 \cdot 2H_2O$ to a warm solution containing 0.001 mol of ligand in 50 ml of ethanol. The resulting solution was filtered and allowed to cool. Slow evaporation deposited dark-brown crystals analyzed as $CuCl_2(C_7H_6N_2S)_2$. Analysis found: C 38.20, N 13.02, H 2.93%; calculated: C 38.67, N 12.88, H 2.78%.

Crystal data

$[CuCl_2(C_7H_6N_2S)_2]$	$D_m = 1.75$ (3) Mg m^{-3}
$M_r = 434.87$	D_m measured by by flotation
Monoclinic, $P2_1$	Mo $K\alpha$ radiation
$a = 6.4430$ (10) Å	Cell parameters from 15
$b = 13.032$ (3) Å	reflections
$c = 9.987$ (2) Å	$\theta = 10.0–15.0°$
$\beta = 106.85$ (2)°	$\mu = 1.96$ mm^{-1}
$V = 802.6$ (3) Å^3	$T = 293$ K
$Z = 2$	Needle, brown
$D_x = 1.799$ Mg m^{-3}	$0.4 \times 0.1 \times 0.1$ mm

Data collection

Siemens *P*3 diffractometer	$R_{int} = 0.026$
ω–2θ scans	$\theta_{max} = 27.6°$
Absorption correction: ψ scan	$h = -8 \rightarrow 8$
(North *et al.*, 1968)	$k = 0 \rightarrow 16$
$T_{min} = 0.721$, $T_{max} = 0.822$	$l = 0 \rightarrow 12$
2096 measured reflections	3 standard reflections
1933 independent reflections	every 50 reflections
1649 reflections with $I > 2\sigma(I)$	intensity decay: none

Refinement

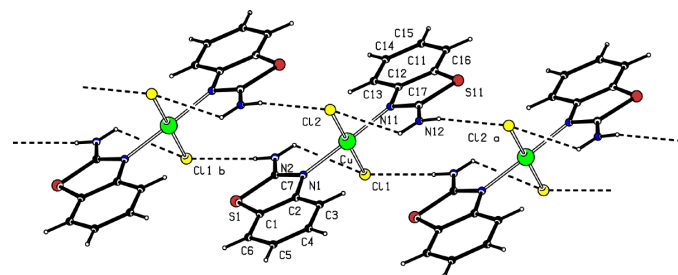|	
Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0445P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.038$	$+ 0.5431P]$
$wR(F^2) = 0.087$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.03$	$(\Delta/\sigma)_{max} < 0.001$
1933 reflections	$\Delta\rho_{max} = 0.96$ e Å^{-3}
209 parameters	$\Delta\rho_{min} = -0.44$ e Å^{-3}
H-atom parameters constrained	Absolute structure: Flack (1983)
	Flack parameter = 0.08 (3)

Figure 2
Diagram showing hydrogen bonds in (I) as dashed lines. [Symmetry codes: (*a*) $1 + x$, y, z; (*b*) $x - 1$, y, z, corresponding to (ii) and (i), respectively, in Table 2.]

Table 1
Selected geometric parameters (Å, °).

Cu—Cl1	2.2747 (19)	Cu—N1	1.986 (5)
Cu—Cl2	2.2969 (19)	Cu—N11	1.988 (5)
Cl1—Cu—Cl2	177.58 (7)	Cl2—Cu—N1	89.98 (19)
Cl1—Cu—N1	89.34 (19)	Cl2—Cu—N11	89.41 (19)
Cl1—Cu—N11	91.32 (19)	N1—Cu—N11	178.7 (2)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N2—H1···Cl1	0.86	2.74	3.266 (6)	121
N2—H2···Cl1^i	0.86	2.48	3.265 (6)	152
N12—H11···Cl2	0.86	2.64	3.202 (6)	124
N12—H12···Cl2^{ii}	0.86	2.54	3.316 (6)	151

Symmetry codes: (i) $x - 1$, y, z; (ii) $1 + x$, y, z.

All H atoms were placed in calculated positions and refined as riding, with $U_{iso}(H) = 1.2U_{eq}(C,N)$.

Data collection: *P3 Software* (Siemens, 1993); cell refinement: *P3 Software*; data reduction: *XDISK* in *SHELXTL/PC* (Sheldrick, 1990); structure solution: *SHELXS*97 (Sheldrick, 1997); structure refinement: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *PLATON*.

References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans.* 2, pp. S1–19.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Giusti, A. & Peyronel, G. (1982). *Spectrochim. Acta A*, **38**, 975–979.
Holm, R. H. & O'Connor, M. J. (1971). *Prog. Inorg. Chem.* **14**, 253–258.
Macíček, J., Davarska, G. H. & Davarski, K. A. (1987). *Z. Kristallogr.* **180**, 157–164.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Raper, E. S. (1994). *Coord. Chem. Rev.* **129**, 91–151.
Sheldrick, G. M. (1990). *SHELXTL/PC Users Manual.* Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.
Siemens (1993). *P3 Software.* Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Sieroń, L. & Bukowska-Strzyżewska, M. (1999). *Acta Cryst.* C**55**, 167–169.
Sieroń, L. & Bukowska-Strzyżewska, M. (2000). *Acta Cryst.* C**56**, 19–21.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
Usman, A., Fun, H.-K., Chantraprommna, S., Zheng, M., Chen, Z. F., Tang, Y. Z., Shib, S. M. & Liang, H. (2003). *Acta Cryst.* E**59**, m41–m43.